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- 12.01 Precursors to Semiconducting Materials**, Pages 1-34, C.J. Carmalt and S. Basharat
- 12.02 From Metal–Organic Precursors to Functional Ceramics and Related Nanoscale Materials**, Pages 35-70, S. Mathur and M. Driess
- 12.03 Organometallic Derived Metals, Colloids, and Nanoparticles**, Pages 71-99, B. Chaudret and K. Philippot
- 12.04 Organometallic Complexes for Optoelectronic Applications**, Pages 101-194, M.E. Thompson, P.E. Djurovich, S. Barlow and S. Marder
- 12.05 Metallomesogens**, Pages 195-293, D.W. Bruce, R. Deschenaux, B. Donnio and D. Guillon
- 12.06 Organometallic Macromolecular Materials**, Pages 295-411, I. Manners
- 12.07 Organometallic Magnetic Materials**, Pages 413-443, E. Coronado, J.R. Galán-Mascarós and J.S. Miller
- 12.08 Medicinal Organometallic Chemistry**, Pages 445-464, G. Jaouen and P. Dyson
- 12.09 Organometallic Receptors for Charged and Neutral Guest Species**, Pages 465-498, P.D. Beer and S.R. Bayly
- 12.10 Surface Organometallic Chemistry**, Pages 499-553, J.-M. Basset, J.-P. Candy and C. Copéret
- 12.11 Organometallic Crystal Engineering**, Pages 555-588, D. Braga, L. Maini, M. Polito and F. Grepioni
- 12.12 Organometallic Compounds in Biosensing**, Pages 589-602, A.E.G. Cass
- 12.13 Environmental and Biological Aspects of Organometallic Compounds**, Pages 603-661, R.O. Jenkins, P.J. Craig, K.A. Francesconi and C.F. Harrington
- 12.14 Polymer-supported Organometallic Catalysts**, Pages 663-753, N.E. Leadbeater

**12.15 Organometallic Clusters**, Pages 755-780, J.B. Keister

**12.16 Organometallic Inclusion and Intercalation Chemistry**, Pages 781-835, E. Monflier, F. Hapiot and D. O'Hare

**12.17 Green Organometallic Chemistry**, Pages 837-864, E.G. Hope, A.P. Abbott, D.L. Davies, G.A. Solan and A.M. Stuart

# 12.01

## Precursors to Semiconducting Materials

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<b>12.01.1</b>	<b>Introduction and Scope</b>	<b>1</b>
<b>12.01.2</b>	<b>Organometallic Precursors for the Growth of III–V Semiconductors</b>	<b>2</b>
12.01.2.1	Introduction—Conventional Precursors	2
12.01.2.1.1	Group III nitrides	2
12.01.2.1.2	Group III phosphides, arsenides, and antimonides	8
12.01.2.2	Single-source Organometallic III–V Precursors	13
12.01.2.2.1	Group III nitride precursors	14
12.01.2.2.2	Group III phosphide, arsenide, and antimonide precursors	20
<b>12.01.3</b>	<b>Organometallic Precursors for the Growth of II–VI Semiconductors</b>	<b>22</b>
12.01.3.1	Introduction	22
12.01.3.2	Conventional and Single-source Approach to II–VI Materials	22
<b>12.01.4</b>	<b>Organometallic Precursors for the Growth of III–VI and IV–VI Semiconductors</b>	<b>25</b>
12.01.4.1	Introduction	25
12.01.4.2	Growth of III–VI semiconductors	25
12.01.4.3	Single-source Organometallic Precursors for IV–VI Materials	28
<b>12.01.5</b>	<b>Organometallic Precursors for the Growth of Ternary Chalcogenide Semiconductors</b>	<b>29</b>
12.01.5.1	Introduction	29
12.01.5.2	Organometallic Precursors for Copper Indium Sulfide	29
12.01.5.3	Organometallic Precursors for Cadmium Zinc Chalcogenides	30
<b>References</b>		<b>30</b>

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### 12.01.1 Introduction and Scope

This chapter deals with organometallic compounds that find application as precursors to semiconductors. Volatile organometallic compounds are being increasingly employed for the deposition of compound semiconductors from the vapor phase by a technique called metalloorganic chemical-vapor deposition (MOCVD). This technique for depositing semiconductor thin films now has several alternative names, including OMCVD (organometallic CVD). The abbreviations MOVPE or OMVPE, in which VPE is defined as vapor-phase epitaxy, are also used to highlight the deposition of homo- or heteroepitaxial layers. In this chapter, the original term MOCVD is adopted. The technique MOCVD involves vapor transport of the metal as a metalloorganic compound. For example, GaAs can be deposited from the pyrolysis of trimethylgallium in the presence of arsine ( $\text{AsH}_3$ ) at 600–800 °C. Typically, the semiconductor alloy is deposited on single crystal wafer substrates such that each layer adopts the same crystalline orientation as the substrate. In order to control the composition of the semiconductor, the concentration of the precursors can be varied in the vapor phase. MOCVD is a complex process, which involves a series of gas-phase and surface reactions. However, the main steps involved are (i) evaporation and transport of the precursors, (ii) formation of the semiconductor alloy via pyrolysis of the precursors, and (iii) removal of decomposition products from the reactor zone. This technique allows precise control of purity, layer thickness, and doping concentrations, and can be used to grow large areas of semiconductor layers. Thus, it can be used to produce multilayer devices.

Aspects of the formation of semiconductors from organometallic compounds have been covered in reviews published since 1994 by Jones,<sup>1</sup> Cowley and Jones,<sup>2</sup> Neumayer and Ekerdt,<sup>3</sup> Gleizes,<sup>4</sup> O'Brien and co-workers,<sup>5,6</sup> Buhro,<sup>7</sup> Maury,<sup>8</sup> and Getman and Franklin.<sup>9</sup> Compound semiconductors have also been deposited using other techniques, such as chemical-beam epitaxy (CBE) and metalloorganic molecular-beam epitaxy (MOMBE). Some

of the precursors employed for the deposition of semiconductors have also been used for the formation of nanoparticles (see Section 12.01.3).

## 12.01.2 Organometallic Precursors for the Growth of III–V Semiconductors

### 12.01.2.1 Introduction—Conventional Precursors

Informative reviews of the growth techniques and structural, optical, and electrical properties and applications of III–V semiconductors have been published by Strite *et al.*,<sup>10</sup> Ambacher,<sup>11</sup> and Jones and O'Brien.<sup>12</sup> Some of the applications of III–V semiconductors are described in Table 1.

This section focuses on the use of organometallic complexes for the deposition of III–V thin films via dual-source routes using conventional precursors. The conventional approach to growing III–V materials is where separate group III and V precursors are combined (Table 2). The metalloorganic precursors traditionally employed are readily available commercially and have convenient vapor pressures. Manasevit first described the use of organometallic compounds to deposit semiconductor films in 1968.<sup>13</sup> These original precursors introduced by Manasevit are still favored today. The volatile group III trialkyls, trimethylgallium ( $\text{Me}_3\text{Ga}$ ), trimethylaluminum ( $\text{Me}_3\text{Al}$ ), and trimethylindium ( $\text{Me}_3\text{In}$ ), in combination with the group V hydride gases (ammonia, phosphine, and arsine) result in III–V layers that contain relatively low levels of carbon contamination. This is due to the large quantity of “active” atomic hydrogen produced by the pyrolysis of the group V hydride gas and thus clean removal of carbon-containing fragments from the growth surface. The optical and electrical properties of semiconductor films grown by techniques such as MOCVD and CBE are critically dependent on the purity and nature of the metalloorganic precursor. For example, the decomposition characteristics heavily influence the incorporation of intrinsic impurities, such as carbon, in the film. Extrinsic impurities, for example, Zn, Si, and solvent, depend on the synthetic and purification routes. Significant developments in metalloorganic precursor technology have been reported in the past 10 years, as discussed below.

#### 12.01.2.1.1 Group III nitrides

The conventional MOCVD of AlN, GaN, and InN involve the reaction of  $\text{Me}_3\text{Al}$ ,  $\text{Me}_3\text{Ga}$ , or  $\text{Me}_3\text{In}$  with ammonia ( $\text{NH}_3$ ).<sup>14</sup> The high thermal stability of  $\text{NH}_3$  results in the need for high substrate temperatures ( $>1,000^\circ\text{C}$ ) and high V/III ratios (e.g., 2,000:1) are required to inhibit nitrogen desorption. Therefore, due to the high temperatures, the choice of substrate material available is limited. Recent reports on the deposition of GaN from  $\text{R}_3\text{Ga}$  and  $\text{NH}_3$  have attempted to overcome the large lattice and thermal mismatches between GaN and most commercially available substrates (e.g., sapphire). This mismatch makes the deposition of single crystal, defect-free materials difficult, as crack formation can occur when the thickness of the grown film exceeds a critical thickness.<sup>15</sup> This, in turn, may be responsible for weak light-emitting diode (LED) light output. However, high-quality GaN films have been obtained on (0001) sapphire substrates by exposing the substrates to  $\text{Me}_3\text{Ga}$  and  $\text{NH}_3$ , one at a time.<sup>16,16a</sup> The best films were obtained at  $800\text{--}900^\circ\text{C}$  with a thin GaN buffer layer pre-deposited at  $500^\circ\text{C}$  and a V/III ratio of 5,000. The formation of high-quality GaN films at relatively lower temperatures than conventional MOCVD has been attributed to the migration enhancement of the Ga adatoms on the grown surface and the easy access of cracked N–H radicals.<sup>16,16a</sup> Similarly, separate admittances of  $\text{Me}_3\text{Al}$  or  $\text{Me}_3\text{Ga}$  and  $\text{NH}_3$  resulted in AlN and GaN films on Si(111) and Si(001)

**Table 1** Applications of III–V semiconductors

III–V Semiconductor	Applications
GaN	Blue light-emitting diodes (LEDs)
GaP	Red LEDs, photocathodes
InP	Weather radar devices, Gunn diodes
GaAs	Solar cells, LEDs
Ga(AsP)	Red LEDs
AlGaAs	Heterostructure lasers, solar cells, field effect transistors (FETs)
InGaN	Green LEDs
InGaP/AlGaInP	Red laser pointers
GaSb/AlGaSb	Thermal imaging devices, environmental sensors
AlGaInP	Yellow/green LEDs

**Table 2** MOCVD of III-V compounds

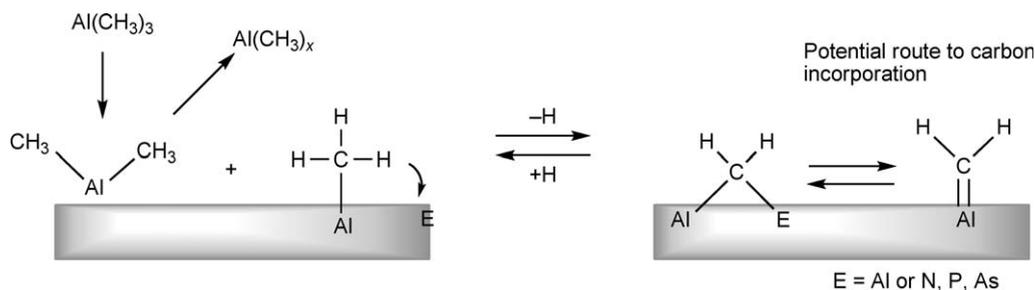
III-V Semiconductor	Reactants	Growth temperature (°C)
AlN	Me <sub>3</sub> Al, NH <sub>3</sub>	1,250
GaN	Me <sub>3</sub> Ga, NH <sub>3</sub>	925–975
GaP	Me <sub>3</sub> Ga, PH <sub>3</sub>	700–800
InP	Me <sub>3</sub> In, PH <sub>3</sub>	650
GaAs	Me <sub>3</sub> Ga, AsH <sub>3</sub>	600–750
Ga(AsP)	Me <sub>3</sub> Ga, AsH <sub>3</sub> , PH <sub>3</sub>	700–725
AlGaAs	Me <sub>3</sub> Al, Me <sub>3</sub> Ga, AsH <sub>3</sub>	650–800
AlAs	Me <sub>3</sub> Al, AsH <sub>3</sub>	700
InGaAs	Me <sub>3</sub> In, Me <sub>3</sub> Ga, AsH <sub>3</sub>	650
InGaAlP	Me <sub>3</sub> In, Me <sub>3</sub> Al, Me <sub>3</sub> Ga, PH <sub>3</sub>	750
AlSb	Me <sub>3</sub> Al, Me <sub>3</sub> Sb	450
GaSb	Me <sub>3</sub> Ga, Me <sub>3</sub> Sb	500–550
InSb	Me <sub>3</sub> In, Me <sub>3</sub> Sb	470
AlGaSb	Me <sub>3</sub> Al, Me <sub>3</sub> Ga, Me <sub>3</sub> Sb	450

substrates at 1,000 °C.<sup>17</sup> The use of buffer layers, including AlN and GaN, lead to a marked improvement in luminescence and electrical properties of GaN and crystalline quality. Thus, high-quality GaN films were achieved by using a high-temperature-grown AlN buffer.<sup>18</sup>

In order to grow GaN films with a lower defect density, silicon carbide (SiC) was chosen as an alternative substrate as it has a relatively small lattice mismatch with GaN. Single-crystalline hexagonal GaN films have been grown on 3C-SiC/Si(111) substrates using a number of buffer layers by MOCVD.<sup>19</sup> The use of buffer layers greatly improved the surface morphology and structural and optical qualities of the GaN film. Thus, well-orientated GaN growth along the *c*-axis with good surface morphology was achieved. Zirconium diboride, ZrB<sub>2</sub>, layers provide an electrically conductive lattice-matched substrate for GaN growth.<sup>20,21</sup> The lattice mismatch between ZrB<sub>2</sub> and GaN on the basal plane is only about 0.6%, compared with 14.9% in the case of sapphire. GaN films were grown on metallic ZrB<sub>2</sub> by MOCVD using Me<sub>3</sub>Ga and NH<sub>3</sub>. Cross-sectional transmission electron microscopy (TEM) showed that when ZrB<sub>2</sub> is exposed to an ammonia atmosphere, cubic ZrB<sub>x</sub>N<sub>1-x</sub> is formed on the surface, which protects the nucleation of GaN. However, high-quality GaN growth was achieved by depositing a very thin AlN (from Me<sub>3</sub>Al and NH<sub>3</sub>) or GaN layer at low temperature.

Surface decomposition pathways for a number of precursors can provide information on reaction mechanisms. This is important as it can lead to more appropriate precursor design and optimized growth conditions. For example, the surface chemistry of two related Al precursors, Me<sub>3</sub>Al and Me<sub>2</sub>AlH, has been studied by high-resolution electron energy loss spectroscopy (HREELS). For both complexes, the dominant surface species at room temperature is based on intact methyl groups, such that Me<sub>2</sub>Al is formed from either loss of a methyl group from Me<sub>3</sub>Al or hydrogen from Me<sub>2</sub>AlH.<sup>22</sup> A surface methylene group (CH<sub>2</sub>) was identified at higher temperatures, which suggests that there is a competing decomposition pathway involving hydrogen abstraction from a surface methyl group (Figure 1).

Further information about the surface chemistry occurring during the MOCVD of AlN was provided by Fourier-transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) studies on mixtures of Me<sub>3</sub>Al

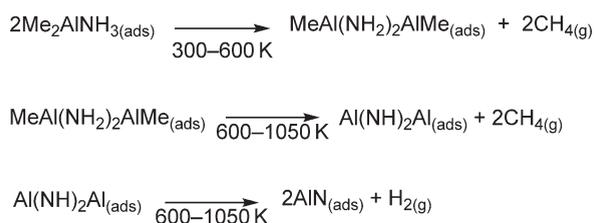
**Figure 1** Mechanism for the proposed decomposition of Me<sub>3</sub>Al on an AIE (E = N, P, or As) surface.

and  $\text{NH}_3$  adsorbed on  $\alpha\text{-Al}_2\text{O}_3$ .<sup>23</sup> These studies suggested that co-adsorption of  $\text{Me}_3\text{Al}$  and  $\text{NH}_3$  at room temperature results in the surface adduct  $[\text{Me}_2\text{AlNH}_3]$  and adsorbed  $\text{NH}_3$ . Increasing the substrate temperature to 600 K and above resulted in the appearance of a vibrational band corresponding to  $\text{AlN}$ , which suggests the formation of extended (Al–N) networks on the surface.  $\text{AlN}$  is then formed by the elimination of  $\text{H}_2$  at the surface from the  $\text{Al}(\text{NH}_2)_2\text{Al}$  species (Scheme 1). This decomposition pathway is the potential route to carbon incorporation during epitaxial growth of III–V semiconductors. In general, greater carbon incorporation in Al-based alloys is observed in comparison to Ga-based alloys. The increased bond strength of Al–C (Al– $\text{CH}_3$  272  $\text{kJ mol}^{-1}$ ) compared with Ga–C (Ga– $\text{CH}_3$  247  $\text{kJ mol}^{-1}$ ) results in an increased number of methyl radicals strongly bound to an Al atom on the substrate surface.

The surface decomposition of  $\text{Et}_3\text{Ga}$  on GaAs(100) has been investigated due to its extensive use in the CVD growth of III–V films.<sup>24</sup> Deuterium labeling indicated that decomposition of the surface ethyl group proceeds exclusively via a  $\beta$ -hydride elimination mechanism (Figure 2). Thus, during hydride elimination, an alkyl group hydrogen is transferred to the surface. This transfer occurs above the temperature where hydrogen desorbs from Ga or As surface sites (480–510 K), and so the surface-bound hydrogen immediately desorbs dissociatively.

$\text{AlN}$  and  $\text{GaN}$  films have been grown on sapphire by laser photochemical vapor deposition at temperatures 600–950 °C (1–5 torr).<sup>25</sup> The precursors  $\text{Et}_3\text{Ga}$  and  $\text{NH}_3$  for  $\text{GaN}$  and  $\text{Me}_3\text{Al}$  and  $\text{NH}_3$  were employed. Photochemical vapor deposition is a direct consequence of the ability of short wavelength radiation ( $\lambda < \sim 300 \text{ nm}$ ) to rupture the chemical bonds in many CVD precursors. Indeed, kinetic modeling of the growth rate dependence on laser pulse energy indicated that the  $\text{NH}_2$  radical is the dominant species, photolytically produced. The growth of (11 $\bar{2}$ 0)-orientated  $\text{GaN}$  films was achieved in the presence of 193 nm photons. Thus, the surface kinetics was being driven by photochemistry in the gas phase. Microwave plasma MOCVD has been used to deposit high-quality  $\text{GaN}$  thin films in a nitrogen–hydrogen microwave plasma.<sup>26</sup> Trimethylgallium was employed as the Ga precursor, and the primary N-atom precursors were speculated to be  $\text{NH}$  radicals. The deposit was identified as stoichiometric  $\text{GaN}$  using XPS and powder X-ray diffraction (XRD) and the material was highly orientated along the  $c$ -axis.

Molecular-beam epitaxy (MBE) is another technique that has been used to grow high-quality  $\text{GaN}$  thin films. Conventional MBE involves the employment of gaseous sources of the elements as precursors. However, a hybrid technique called MOMBE has been developed, which uses metalloorganic species for the group III elements combined with plasma-activated nitrogen or ammonia for the group V species.<sup>27</sup> MOMBE of  $\text{GaN}$  has been achieved using  $\text{Me}_3\text{Ga}$  or  $\text{Et}_3\text{Ga}$  combined with atomic nitrogen from a plasma source or ammonia. During the growth of  $\text{GaN}$ , these reactive nitrogen species can react with the decomposition products of the trialkylgallium to form volatile compounds, which effectively reduce the growth rate. The loss of active nitrogen has been suggested to be due to the formation of ammonia from a reaction between hydrogen and active nitrogen and the formation of hydrogen cyanide through a reaction between hydrogen, carbon, and nitrogen. The formation of



Scheme 1

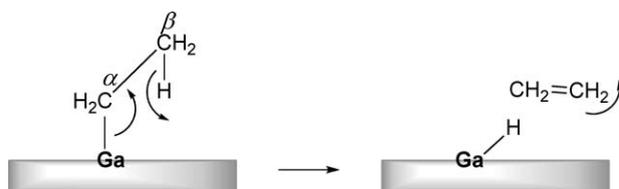


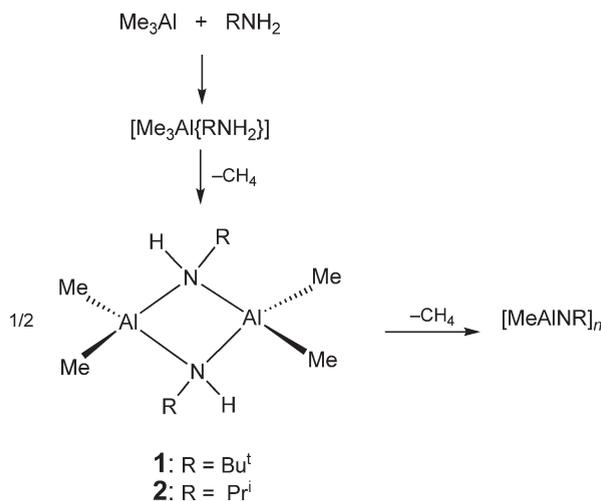
Figure 2  $\beta$ -Hydride elimination from a coordinated ethyl group to give ethylene and surface-bound hydrogen.

ethenylamine via reaction of active nitrogen and ethyl radicals from  $\text{Et}_3\text{Ga}$  was observed when triethylgallium was employed as the Ga source. The above could also account for carbon incorporation during the growth of GaN. In the past 10 years, much effort has also been put toward the development of III–V materials technology grown from trialkylgroup III species and group V trihydrides, including violet-blue GaN LEDs,<sup>28</sup> InGaN/AlGaIn double-heterostructure blue LEDs,<sup>29,30</sup> InGaIn/GaN LEDs,<sup>31,32,33</sup> AlGaIn<sup>34</sup> and AlGaIn/GaN heterostructure field effect transistor (HFET).<sup>35</sup>

Single-source precursors, of the type  $[\text{Me}_2\text{MN}(\text{H})\text{R}]_n$ , have been employed for the deposition of semiconductor films (Section 12.01.2.2.1). The successful formation of semiconductor films from these compounds resulted in the use of similar species formed *in situ* in the vapor phase prior to layer growth.<sup>36</sup> The aim of the method was to combine the advantages of low growth temperatures typical in the use of single-source precursors with the high growth rates associated with high vapor pressure reagents. Atmospheric pressure (AP)CVD of  $\text{Me}_3\text{Al}$  and the volatile primary alkylamines,  $\text{Bu}^t\text{NH}_2$  and  $\text{Pr}^i\text{NH}_2$ , at 400–600 °C afforded AlN films with variable levels of residual carbon and oxygen present (4.7–17.0 at.% by auger electron spectroscopy (AES)). Post-growth oxidation of the amorphous AlN films was the cause of the oxygen contamination. However, the carbon impurities were attributed to the decomposition of surface-adsorbed methyl radicals derived from  $\text{Me}_3\text{Al}$ . The mechanism of AlN growth from  $\text{Me}_3\text{Al}$  and  $\text{RNH}_2$  ( $\text{R} = \text{Bu}^t$  or  $\text{Pr}^i$ ) was proposed to proceed via the gas-phase formation of elimination products, such as  $[\text{Me}_2\text{AlN}(\text{H})\text{R}]_2$  (**1**,  $\text{R} = \text{Bu}^t$ ; **2**,  $\text{Pr}^i$ ), prior to film deposition (Scheme 2). The *t*-butyl and *i*-propyl group may be eliminated via  $\beta$ -hydride elimination when these complexes are pyrolyzed on or near the substrate. The result of this would be the formation of intramolecular Al–N bonds and growth of stoichiometric AlN. Support for this mechanism was obtained by the formation of AlN directly from compounds **1** and **2** (Section 12.01.2.2.1).<sup>37</sup> Interestingly,  $\text{Bu}^t\text{NH}_2$  and  $\text{R}_3\text{Ga}$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ) did not result in the formation of GaN and only droplets of Ga metal were formed.<sup>38</sup> This was attributed to the weaker Lewis acidity of  $\text{R}_3\text{Ga}$  in relation to  $\text{Me}_3\text{Al}$ , which in turn would result in the dissociation of any adducts rather than elimination reactions.<sup>39,39a,39b</sup>

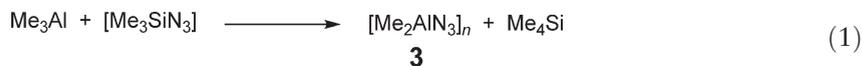
In an attempt to reduce the carbon contamination in AlN films,  $\text{Bu}^t\text{NH}_2$  was used in combination with  $\text{Bu}^t\text{Al}$ .<sup>40</sup> Atmospheric pressure MOCVD at 500–600 °C afforded AlN films, which on deposition of a protective Al overlayer by pyrolysis of  $\text{Bu}^t\text{Al}$  at 400 °C, resulted in the prevention of post-growth oxidation of the films. AES indicated that the AlN films contained residual carbon (4.7–7.2 atom.%), and thus  $\text{Bu}^t\text{Al}$  has no significant advantages over  $\text{Me}_3\text{Al}$  for growth of AlN from  $\text{R}_3\text{Al}/\text{RNH}_2$  mixtures. These results suggest that the decomposition of the organic radical of  $\text{RNH}_2$  may play an important role in carbon incorporation since high-purity Al films have been deposited from  $\text{Bu}^t\text{Al}$ .<sup>41</sup>

Trimethylsilylazide ( $\text{Me}_3\text{SiN}_3$ ) has been utilized as an alternative nitrogen source for the formation of AlN films, when used in combination with  $\text{Me}_3\text{Al}$ .<sup>42</sup> AlN films were deposited by atmospheric pressure MOCVD at 300–450 °C, and notably no silicon was detected by AES. The proposed mechanism for the formation of AlN from  $\text{Me}_3\text{SiN}_3$  and  $\text{Me}_3\text{Al}$  involved the formation of  $[\text{Me}_2\text{AlN}_3]$  **3** in the gas phase with concomitant production of tetramethylsilane



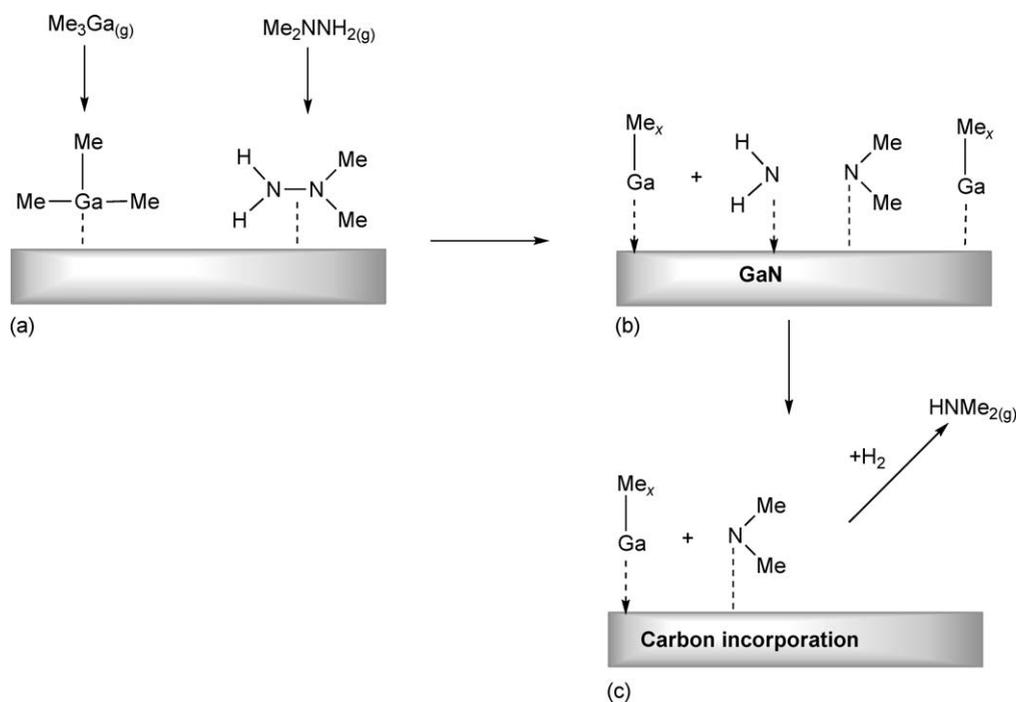
Scheme 2

( $\text{Me}_4\text{Si}$ ), according to Equation (1). Carbon was present at a level of 9.8%, probably due to the decomposition of Al–Me groups on or near the substrate.

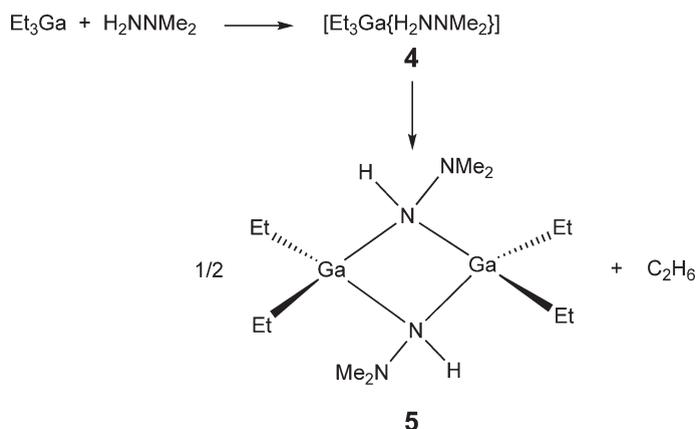


Tetramethylsilane is a relatively stable species, which would be unlikely to be pyrolyzed below  $450^\circ\text{C}$ , and so Si would be transported effectively away from the growth zone. Support for the proposed mechanism was obtained from the *ex situ* reaction of  $\text{Me}_3\text{SiN}_3$  and  $\text{Me}_3\text{Al}$ , which produced  $\text{Me}_4\text{Si}$ , as detected by mass spectroscopy.<sup>42</sup> Interestingly, the attempted formation of GaN from  $\text{Me}_3\text{SiN}_3$  and  $\text{Me}_3\text{Ga}$  was unsuccessful. This is presumably due to the weaker Lewis acidity of  $\text{Me}_3\text{Ga}$  relative to  $\text{Me}_3\text{Al}$ . In contrast, epitaxial GaN films have been grown by low-pressure (LP) CVD (LPCVD) from hydrazoic acid ( $\text{HN}_3$ ) and  $\text{Et}_3\text{Ga}$ .<sup>43</sup> This method of depositing epitaxial films is superior to the traditional routes (using trialkylgallium and  $\text{NH}_3$ ) for two main reasons. First, the labile nitrogen source,  $\text{HN}_3$ , results in lower temperature deposition ( $600$  vs.  $>800^\circ\text{C}$ ). Second, the III/V ratios employed were 1:5, whereas growth techniques involving  $\text{NH}_3$  require ratios of at least 1:2,000. The GaN films produced from  $\text{Et}_3\text{Ga}$  and  $\text{HN}_3$  crystallized in the expected wurtzite structure and were slightly polycrystalline. However, due to the toxic and explosive nature of hydrazoic acid, this method has not found widespread application.

Dimethylhydrazine ( $\text{Me}_2\text{NNH}_2$ ) was thought to be an attractive nitrogen source because it has a lower decomposition temperature (50% decomposition occurs at  $550^\circ\text{C}$ ) than ammonia, which is only 30% decomposed at  $900^\circ\text{C}$ . Growing GaN by MOCVD from the reaction of  $\text{Me}_3\text{Ga}$ <sup>44,45</sup> or  $\text{Et}_3\text{Ga}$ <sup>46,47</sup> and  $\text{Me}_2\text{NNH}_2$  was found to be similar to the growth of GaN using ammonia with respect to growth scheme and temperatures. For example, at temperatures above  $900^\circ\text{C}$ , smooth epitaxial films could be obtained via a two-dimensional growth mode. At lower temperatures, GaN was deposited but growth proceeded in three dimensions resulting in rough surfaces. A similar growth pattern was observed when  $\text{NH}_3$  was used as the group V source. The proposed film growth mechanism is depicted in Figure 3.<sup>48</sup> The first step involves the diffusion of  $\text{Me}_3\text{Ga}$  and  $\text{Me}_2\text{NNH}_2$  molecules from the gas phase to the surface of the substrate. The adsorbed  $\text{Me}_3\text{Ga}$  and  $\text{Me}_2\text{NNH}_2$  molecules on the surface sites are in equilibrium with their own native gaseous molecules and then reaction occurs to form GaN, probably via intermediate species of the type  $\text{Me}_2\text{Ga}$ ,  $\text{MeGa}$ ,  $\text{NH}_2$ , and  $\text{NMe}_2$ . Thus, the reaction of  $\text{Me}_2\text{Ga}$  and  $\text{NH}_2$  was



**Figure 3** Proposed film-growth mechanism of GaN from  $\text{Me}_3\text{Ga}$  and  $\text{Me}_2\text{NNH}_2$ : (a) diffusion and surface adsorption; (b) surface reaction to form GaN; (c) carbon incorporation or reaction with  $\text{H}_2$ .



Scheme 3

proposed to be the main route for GaN growth due to smaller steric hindrance. Carbon incorporation in the films was assumed to be due to both MeGa and NMe<sub>2</sub>. However, the introduction of H<sub>2</sub> would reduce carbon via reaction with NMe<sub>2</sub> to form stable species such as dimethylamine, which in turn could desorb away from the substrate surface.

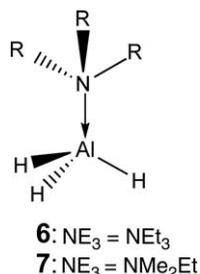
Co-pyrolysis of Me<sub>2</sub>NNH<sub>2</sub> and Et<sub>3</sub>Ga in H<sub>2</sub> at ambient temperature indicated that an adduct and intermediate dimer are formed at low temperatures, as shown in Scheme 3.<sup>49</sup> The dimers began to decompose at 400 °C with the production of ammonia and the decomposition completed at 850 °C. Evidence for the formation of a similar adduct between Me<sub>3</sub>Ga and Me<sub>2</sub>NNH<sub>2</sub> was also obtained from pyrolysis studies.<sup>50</sup>

Epitaxial GaN layers were grown from Me<sub>3</sub>Ga and Bu<sup>t</sup>NNH<sub>2</sub> at 923–958 K by MOCVD.<sup>51,52</sup> Interestingly, films deposited using Bu<sup>t</sup>NNH<sub>2</sub> have much less carbon content than those using MeNNH<sub>2</sub>. This result is due to β-hydride elimination of the *t*-butyl ligand of Bu<sup>t</sup>NNH<sub>2</sub> to form a stable hydrocarbon species.<sup>53</sup> Low-temperature atomic layer growth (ALG) of AlN has been achieved on Si(100) using MeNNH<sub>2</sub> and [AlH<sub>3</sub>{NMe<sub>2</sub>Et}] **6**.<sup>54</sup> The technique of ALG involves flowing the source gases into the reactor in separate, sequential steps. Exposure temperatures of 660 K for MeNNH<sub>2</sub> and 420 K for compound **6** were selected. The growth was suggested to proceed through the dehydrogenation of AlH<sub>x</sub>NH<sub>y</sub> species generated during the ALG of AlN from MeNNH<sub>2</sub> and compound **6**.

1,1-Dimethylhydrazine has been used successfully as a liquid-phase nitrogen precursor for the growth of the cubic phase of GaN (from Me<sub>3</sub>Ga and Me<sub>2</sub>NNH<sub>2</sub>) on GaAs (deposited from Me<sub>3</sub>Ga and AsH<sub>3</sub><sup>55,56</sup> or Bu<sup>t</sup>AsH<sub>2</sub>).<sup>57,58</sup> In addition, the growth of a range of alloys at low temperature has been achieved using Me<sub>2</sub>NNH<sub>2</sub>, including GaN<sub>x</sub>P<sub>1-x</sub>,<sup>59</sup> GaN<sub>x</sub>As<sub>1-x</sub>,<sup>60,60a–60c,61</sup> InN<sub>x</sub>As<sub>1-x</sub>,<sup>62</sup> GaInNAS,<sup>63,63a–63c</sup> and GaAsSbN.<sup>64</sup> Group III sources employed were Me<sub>3</sub>Ga, Et<sub>3</sub>Ga, or Me<sub>3</sub>In and group V included Me<sub>2</sub>NNH<sub>2</sub>, PH<sub>3</sub>, Bu<sup>t</sup>AsH<sub>2</sub>, AsH<sub>3</sub>, Me<sub>3</sub>Sb, and Et<sub>3</sub>Sb, depending upon which alloy was grown. Gallium nitride passivation layers have also been grown *in situ* on near-surface In<sub>x</sub>Ga<sub>1-x</sub>As/GaAs quantum wells from Me<sub>3</sub>Ga, Me<sub>3</sub>In, and Bu<sup>t</sup>AsH<sub>2</sub> using Me<sub>2</sub>NNH<sub>2</sub> as the nitrogen source.<sup>65</sup> However, the combustion or decomposition of dimethylhydrazine is strongly exothermic, causing a potential safety hazard and restricting its widespread use in MOCVD. Furthermore, nitrogen trifluoride and hydrazine have been shown to be more efficient nitrogen sources than unsymmetrical dimethylhydrazine for the growth of GaAsN and (In)GaAsN (from Et<sub>3</sub>Ga or Me<sub>3</sub>Ga, Me<sub>3</sub>In, and AsH<sub>3</sub>).<sup>66</sup>

Trialkylaluminum compounds, such as Et<sub>3</sub>Al and Me<sub>3</sub>Al, are the most commonly used metalloorganic Al sources. However, trialkylaluminum compounds are characterized by the presence of Al–C bonds which can lead to significant levels of trace carbon in the resulting semiconductor films. The carbon is thought to be the result of decomposition of methyl radicals (Figure 1) strongly bound to an Al atom on or adjacent to the growth surface.<sup>67</sup> Efforts to overcome this problem include the use of amine adducts of alane (AlH<sub>3</sub>). Thus, the reaction of trimethylamine alane [AlH<sub>3</sub>{NMe<sub>3</sub>}] **7** with NH<sub>3</sub> was shown to afford AlN at temperatures as low as 127 °C.<sup>68</sup> Annealing at temperatures above 900 °C resulted in greater AlN formation but with chemisorbed NH<sub>2</sub> remaining on the surface. However, the high reactivity and low decomposition temperature of compound **7** can lead to enhanced gas-phase reactions and particle formation, non-uniform deposition on the substrate, and reactant depletion.<sup>69</sup> In order to use alane adducts for the deposition of semiconductor films, techniques that minimize interaction of reactants in the gas phase must be utilized. One method is low-pressure MOCVD where the gas-phase interactions are limited at reduced pressure. An

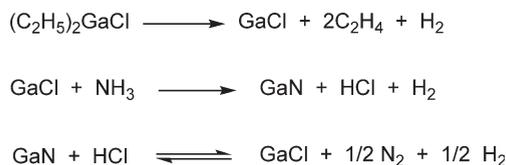
alternative is the application of ALG and both techniques have been employed for the deposition of AlN films from compound **6** and NH<sub>3</sub>. Using ALG, the Al precursor **6** and NH<sub>3</sub> were delivered to the growth surface in separate steps in order to promote film formation through a sequence of surface reactions.<sup>70</sup> AlN films were deposited on a range of substrates (Si(100), Si(111), Al<sub>2</sub>O<sub>3</sub>) at 250–450 °C and were found to have carbon and oxygen contamination at the surface and smaller concentrations in the bulk film. By XPS, the N(1s) data showed the presence of chemically bonded H in the films as NH<sub>3-x</sub> (x = 0–2) species. The reaction of NH<sub>3</sub> with **6** was found to be incomplete at temperatures below 277 °C resulting in unreacted NH<sub>x</sub> species, but above 327 °C, the NH<sub>x</sub> concentration was lower.



MOCVD of GaN commonly uses trialkylgallium and NH<sub>3</sub>, with or without a H<sub>2</sub> carrier gas. In contrast, hydride vapor-phase epitaxy (HVPE) utilizes GaCl generated *in situ* via the reaction of liquid Ga with HCl in a hot zone. This technique has the advantages of high throughput and easy scaling to large wafer dimensions. However, slow gas-phase switching times have restricted the application of HVPE. Diethylgallium chloride, [Et<sub>2</sub>GaCl], has been employed as the gallium precursor in the epitaxial growth of GaN, which produces a HVPE-like growth chemistry in an MOCVD system.<sup>71</sup> A two-step growth process was employed, which involved the deposition of a low-temperature GaN buffer layer from [Et<sub>2</sub>GaCl] and NH<sub>3</sub>, followed by high-temperature epitaxial growth of GaN. The growth rate decreased with increasing growth temperature, which has been attributed to a thermodynamic equilibrium limitation at the growth front. Additional reaction pathways are provided at the growth surface due to the presence of chlorine in the growth chemistry. The gas-phase reactions at the GaN growth front can be summarized, as shown in Scheme 4. The last reaction in Scheme 4 suggests an equilibrium between the steady-state concentrations of HCl and GaCl at the growth front. This reaction was thought to be the cause of the different surface morphology of the films formed from [Et<sub>2</sub>GaCl] compared to those deposited from Et<sub>3</sub>Ga. These reactions would provide reaction pathways for the removal of surface structure along with chemical defects and impurities.

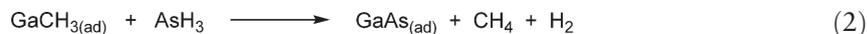
#### 12.01.2.1.2 Group III phosphides, arsenides, and antimonides

The conventional precursors employed for the deposition of group III phosphides and arsenides (Table 2) are the group III trialkyl species in combination with the group V hydride gases, arsine (AsH<sub>3</sub>) and phosphine (PH<sub>3</sub>). Although much of the research on the CVD reactions of R<sub>3</sub>M and EH<sub>3</sub> has been published prior to 1994 (COMC (1995)), studies are still being conducted to understand the mechanism and surface chemistry of these reactions. A kinetic model based on the collision theory of chemical reactions has been proposed for the MOCVD of GaAs from Me<sub>3</sub>Ga and AsH<sub>3</sub>.<sup>72</sup> This model suggests that four heterogeneous deposition reactions occur: As-containing and Ga-containing species with As and Ga sites, as well as C-incorporation reactions. The surface reactions and kinetic phenomena of GaAs monomolecular layer growth using chemical adsorption of Me<sub>3</sub>Ga and AsH<sub>3</sub> have been studied.<sup>73</sup> Molecular layer epitaxy (MLE) can produce single crystalline films, monolayer by monolayer, by injection of component gases of the materials, alternatively, onto the substrate in an ultrahigh vacuum (UHV) chamber. It was observed that the growth rate per cycle was greatly influenced by the surface stoichiometry of arsenic during growth.



Scheme 4

The adsorption species was concluded to be GaCH<sub>3</sub> under monolayer growth conditions, as detected by a real time optical monitoring method.<sup>74</sup> A possible reaction of GaCH<sub>3</sub> with AsH<sub>3</sub> was proposed, as shown in Equation (2).

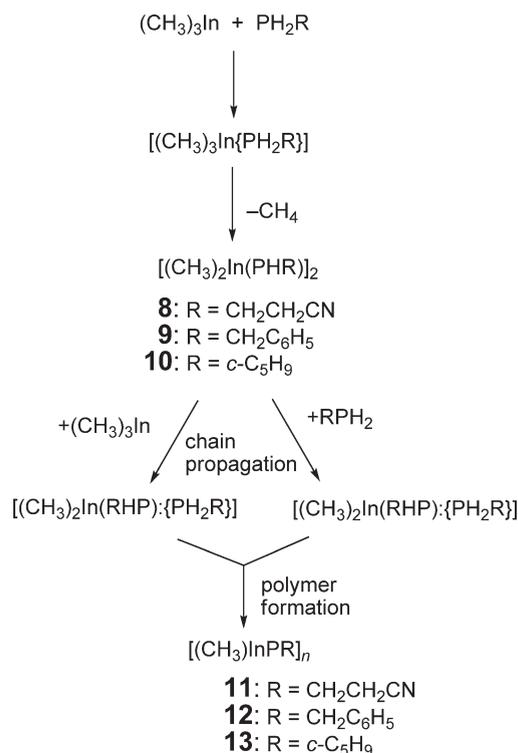


Further information about the surface mechanisms was obtained from the *in situ* study of GaAs growth from Me<sub>3</sub>Ga and Et<sub>3</sub>Ga precursors by MOCVD. During growth with a constant AsH<sub>3</sub> partial pressure, three different phases were observed by reflectance anisotropy spectroscopy (RAS).<sup>75,76</sup> At high temperatures, all the processes on the surface are fast compared to the time for the growth of one monolayer. Kinetic limited growth was observed at low temperature where the surfaces are covered by adsorbates from undecomposed precursors. These prevent attachment and lower the growth rate causing increased carbon incorporation. At intermediate temperatures, the surfaces become Ga-rich during growth in the mass transport limited regime. Detailed studies into the dependence of carbon incorporation on growth conditions for group III arsenides grown with trimethylgroup III complexes and arsine have also been reported in the past 10 years.<sup>77</sup> To attempt to lower the carbon contamination, alternative group III sources have been explored, such as triisopropylgallium as the Ga source.<sup>78</sup> It was found that carbon-doping levels were at least two orders of magnitude lower than those in GaAs layers grown under similar conditions using Me<sub>3</sub>Ga. In addition, the formation of heterostructures, such as InGaP/GaAs, using PH<sub>3</sub> and AsH<sub>3</sub> has been studied.<sup>79</sup> The growth of abrupt GaAs/InGaP/GaAs heterojunctions by MOCVD is difficult because of the intermixing of arsenic and phosphorus at the heterointerfaces.<sup>80</sup>

Much of the recent research has been aimed at developing safer liquid group V precursors for use in MOCVD of III–V materials. Both AsH<sub>3</sub> and PH<sub>3</sub> are extremely toxic gases and are generally stored in high-pressure cylinders such that there is a risk of toxic release during transport. To overcome transport problems, the use of on-site electrochemical generation of AsH<sub>3</sub> using a commercially available arsine generator has been investigated.<sup>81</sup> Epitaxial GaAs was deposited using Me<sub>3</sub>Ga and the generated AsH<sub>3</sub>. The AsH<sub>3</sub> is generated on-site and at-point-of-use from the electrolytic conversion of solid As source material, which substantially improves the safety of the MOCVD process in two ways. First, the AsH<sub>3</sub> is generated when needed, and second, only a small volume of AsH<sub>3</sub> is present. However, alternative group V precursors have been developed in an attempt to replace the group V hydride gases. A highly successful alternative to PH<sub>3</sub> is *t*-butylphosphine (Bu<sup>t</sup>PH<sub>2</sub>), although other primary alkyl phosphines (RPH<sub>2</sub>) have been utilized.<sup>82,83</sup> High quality layers at significantly lower V/III ratios were deposited using Bu<sup>t</sup>PH<sub>2</sub>, and it is less hazardous than phosphine.<sup>84,85</sup> The thermal decomposition of a number of phosphines in the presence of Me<sub>3</sub>In showed that the decomposition led to the formation of PH<sub>3</sub> and hydrocarbons either via a  $\beta$ -hydride or free-radical mechanism.<sup>82</sup> The onset of decomposition occurred at 350 °C for cyanoethylphosphine, 250 °C for benzylphosphine, and 300 °C for cyclopentylphosphine. However, premature reaction with Me<sub>3</sub>In occurred with all of these phosphines at room temperature, resulting in the evolution of CH<sub>4</sub> and the deposition of an involatile liquid or solid. In contrast, Bu<sup>t</sup>PH<sub>2</sub> does not pre-react with Me<sub>3</sub>In and thus, has superior gas-phase chemistry for the deposition of III–V materials. The involatile product was proposed to comprise of polymers of generic formula [MeInPR]<sub>*n*</sub> (**11**, R = CH<sub>2</sub>CH<sub>2</sub>CN; **12**, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>; **13**, *c*-C<sub>5</sub>H<sub>9</sub>), which result via [Me<sub>2</sub>In(PHR)]<sub>2</sub> **8–10**, from mixtures of Me<sub>3</sub>In and RPH<sub>2</sub>. A general mechanism for the proposed pre-reaction is presented in Scheme 5.

In contrast, Bu<sup>t</sup>PH<sub>2</sub> is sufficiently bulky, due to the *t*-butyl group, to both shield and deactivate the In center in the species [Me<sub>2</sub>InP(H)R]. Further attack by other Bu<sup>t</sup>PH<sub>2</sub> molecules is inhibited, preventing chain propagation and polymer formation. Overall, Bu<sup>t</sup>PH<sub>2</sub> is a suitable alternative to PH<sub>3</sub>, can be stored in bubblers at room temperature, and mounted directly onto an MOCVD system. Furthermore, Bu<sup>t</sup>PH<sub>2</sub> exhibits higher incorporation efficiency than PH<sub>3</sub>, and so lower V/III ratios and substrate temperatures can be employed. A range of III/V phosphides have been deposited from the relevant trialkyl group III complex and Bu<sup>t</sup>PH<sub>2</sub>, including InP,<sup>86,87</sup> AlInP, AlInGaP,<sup>88,88a,88b</sup> InP/InGaAsP,<sup>89,90</sup> and GaAsP.<sup>91</sup> Interestingly, under self-limiting growth conditions, it was found that the carbon concentration in InP layer grown using Me<sub>3</sub>In and Bu<sup>t</sup>PH<sub>2</sub> was almost the same as using Et<sub>3</sub>In and Bu<sup>t</sup>PH<sub>2</sub>.<sup>92</sup>

Cyclohexylphosphine (*c*-C<sub>6</sub>H<sub>11</sub>PH<sub>2</sub>) has also been utilized as a group V source to InP.<sup>93</sup> Thus, LPCVD of Me<sub>3</sub>In and *c*-C<sub>6</sub>H<sub>11</sub>PH<sub>2</sub> resulted in the formation of polycrystalline InP films on both Si and InP(100) substrates at temperatures above 580 °C. Pre-cracking of *c*-C<sub>6</sub>H<sub>11</sub>PH<sub>2</sub> at 800 °C causes the phosphine to decompose via a  $\beta$ -hydride elimination pathway to yield *in situ* PH<sub>3</sub> and cyclohexene. The V/III ratio precursor ratios were varied from 4.5 to 179.1 and improved surface morphology was observed for higher V/III ratios.



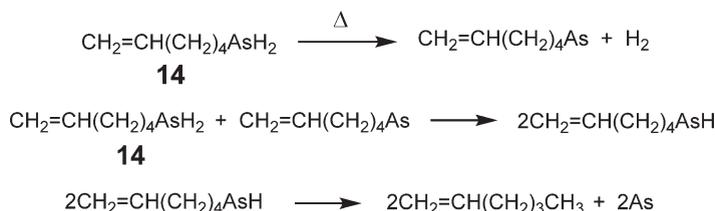
Scheme 5

A novel approach to InP films involved the reaction between the indium(I) precursor  $[\text{In}(\text{C}_5\text{Me}_5)]$  and white- $\text{P}_4$  by MOCVD.<sup>94</sup> The advantages of the reagents  $[\text{In}(\text{C}_5\text{Me}_5)]$  and  $\text{P}_4$  include the following.

- (i) Pre-reactions should be limited because In(I) derivatives have no tendency to form adducts with Lewis bases, such as phosphine.
- (ii) Low-temperature (100–300 °C) epitaxial growth is possible, and so interdiffusion of epitaxial layer should not occur.
- (iii) The high thermal stability of the pentamethylcyclopentadienyl group and the low reaction temperature should minimize the degradation of this organic substituent. Thus, the incorporation of carbon into the growing film should be prevented.

Epitaxial InP films were grown from  $[\text{In}(\text{C}_5\text{Me}_5)]$  and  $\text{P}_4$  at 150–250 °C on InP substrates with a growth rate of 2–34 Åmin<sup>-1</sup>. The low growth rate was attributed to either the low volatility of  $[\text{In}(\text{C}_5\text{Me}_5)]$  and/or the low dissociation rate of  $\text{P}_4$ . The growth rate was improved either by substituting white- $\text{P}_4$  for  $\text{PH}_3$  or using a  $\text{P}_4$ -cracking furnace. Although  $[\text{In}(\text{C}_5\text{Me}_5)]$  has a low sublimation temperature (55 °C at 0.001 torr) and is non-pyrophoric, it is extremely reactive to oxygen and water, which would limit its widespread use in MOCVD.

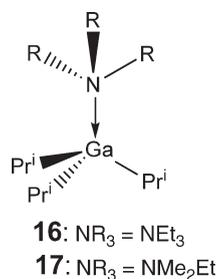
Primary alkylarsines,  $\text{RAsH}_2$ , have been studied as potential replacements to  $\text{AsH}_3$ . Pyrolysis of hex-5-enylarsine,  $\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{AsH}_2$  **14** at 600 °C *in vacuo* resulted primarily in the formation of hex-1-ene,  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_3$ .<sup>95</sup> The proposed mechanism for the decomposition of compound **14** involves the loss of  $\text{H}_2$ , as shown in Scheme 6. The next step consists of a bimolecular reaction between  $\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{As}$  and **14**,



Scheme 6

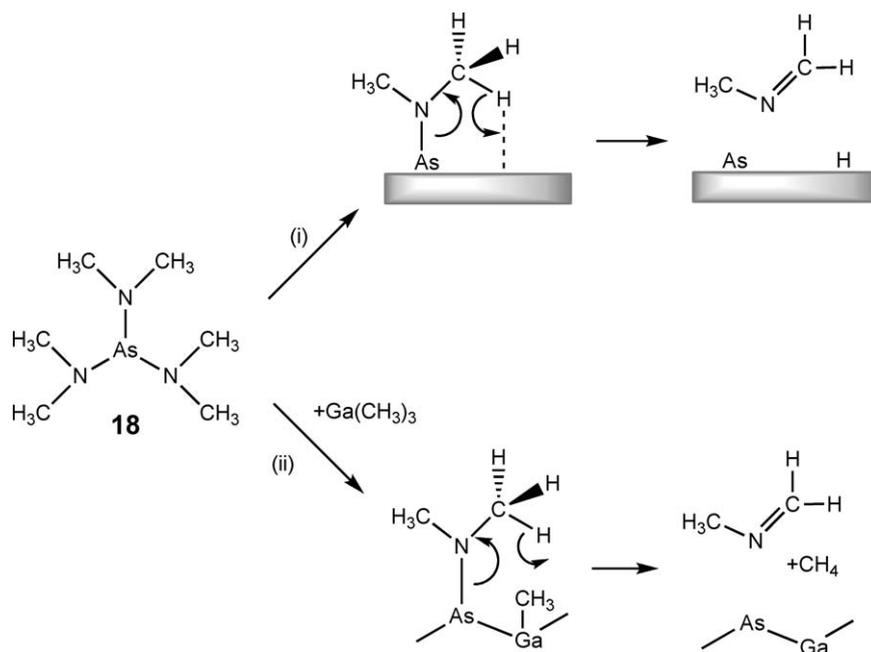
resulting in the reductive elimination of hex-1-ene. In an  $H_2$  atmosphere at room temperature, the reaction of  $Me_3Ga$  and compound **14** resulted in the elimination of  $CH_4$  and the formation of a white solid, which was proposed to be  $[Me_2GaAs((CH_2)_4CH=CH_2)H]_3$  **15**. However, above  $350^\circ C$ , pyrolysis of  $Me_3Ga$  and  $CH_2=CH(CH_2)_4AsH_2$  produced  $Me_2AsH$ ,  $MeAsH_2$ , cyclohexane, and methylenecyclopentane, suggesting a stepwise free-radical decomposition mechanism. The mechanism shown in Scheme 6 does not account for the ability of  $RAsH_2$  precursors to remove surface alkyl radicals and suggests that As atoms may be produced near or at the growth surface. This is in contrast to experimental data for GaAs growth using  $RAsH_2$ .

The most successful replacement for  $AsH_3$  is tertiarybutylarsine ( $Bu^tAsH_2$ ) as it is a liquid and has a convenient vapor pressure of 81 torr at  $10^\circ C$ . Interestingly, experiments have shown a reduction in both O and C concentrations for GaAs and AlGaAs grown using  $Bu^tAsH_2$  when compared to materials grown with  $AsH_3$ .<sup>96</sup> Thus, high-quality films of GaAs and AlGaAs have been grown from  $Me_3Ga$ ,  $Me_3Al$ , and  $Bu^tAsH_2$  by MOCVD at  $640\text{--}700^\circ C$ .<sup>97</sup> It was observed that an increase in the V/III ratio caused a decrease in the growth rates of both GaAs and AlGaAs when using  $Bu^tAsH_2$ , which can be attributed to the excess group V species competing with group III atoms for group III surface sites. The carbon incorporation in AlGaAs films grown using  $Bu^tAsH_2$  was found to be significantly lower than in layers deposited from arsine under higher V/III ratios and/or lower temperature conditions.<sup>98</sup> These studies indicate that the carbon originates from  $Me_3Ga$  and  $Me_3Al$  and not  $Bu^tAsH_2$ .<sup>99</sup> AlGaAs films have also been grown using CBE from triisopropylgallium ( $Pr^i_3Ga$ ) and compound **7**. Trace quantities of diethyl ether in  $Pr^i_3Ga$  from the metalloorganic synthetic procedure can cause oxygen contamination, and by minimizing the concentration of diethyl ether, dramatic improvements in the AlGaAs purity were observed, particularly in terms of oxygen incorporation.<sup>100</sup> An alternative is to eliminate diethyl ether from the synthesis route, and adducts, of the type  $[Pr^i_3Ga\{NR_3\}]$  (**16**,  $NR_3 = NEt_3$ ; **17**,  $NMe_2Et$ ), have been prepared from the reaction between gallium trihalide and  $Pr^iMgBr$  in trialkylamine solvent.<sup>101</sup> The use of compound **16** in combination with **7** leads to AlGaAs of improved purity.



Atomic layer epitaxy (ALE) of GaAs has been achieved using the gallium precursors  $Me_3Ga$ ,  $Et_3Ga$ , and trisneopentylgallium,  $[(CH_3)_3CCH_2]_3Ga$ , in combination with  $Bu^tAsH_2$  at  $470\text{--}550^\circ C$ .<sup>102,103</sup> Both  $Me_3Ga$  and  $[(CH_3)_3CCH_2]_3Ga$  are self-limiting precursors due to the presence of methyl radicals during the growth process.<sup>104</sup> Differences in the surface structures were found between self-limiting and non-self-limiting conditions. In the former, well-defined terraces without droplets were observed. In contrast, the surface morphology of a non-self-limiting surface prepared from  $Et_3Ga$  showed the presence of droplets. For  $[(CH_3)_3CCH_2]_3Ga$ , the first step of the decomposition involves the pyrolytic fission of a Ga–neopentyl bond, and subsequent reactions of the molecule, including  $\beta$ -methyl elimination, result in a methyl radical attached to the surface. In contrast,  $Et_3Ga$  decomposes via  $\beta$ -hydride elimination, and a breakdown of self-limiting behavior occurs.

Tertiarybutylarsine has also been used for the growth of InAs/GaAs heterostructures,<sup>105,106</sup> InAs quantum dots,<sup>107</sup> InAs/InP single quantum well (QW) structures,<sup>108</sup> InGaAs/GaAs quantum dot lasers,<sup>109</sup> InGaAsP/InGaAs multiple step QW structure,<sup>110,111</sup> and InGaAsP/GaAs single QW laser diode structures.<sup>112</sup> In all cases,  $Bu^tAsH_2$  was used in combination with the relevant trialkylgroup III species. CBE of AlAs with  $Me_3Al$ ,  $Bu^tAsH_2$ , or  $As(NMe_2)_3$  **18** at  $750^\circ C$  showed significant differences in the resulting films.<sup>113</sup> Rough growth surfaces and films of poor crystal quality were obtained from growth with  $Bu^tAsH_2$ , whereas streaky patterns were observed with compound **18**. The growth rate was found to increase with increasing group V flux. Similarly, p-type GaAs films have been grown by CBE using compound **18** and  $Me_3Ga$ .<sup>114</sup> The use of **18** as the As source leads to a significant reduction in carbon contamination in GaAs and AlGaAs films grown by CBE, even in combination with methyl-based precursors.<sup>115</sup> The decomposition of compound **18** involves the formation of *N*-methylene imine and surface hydrogen via  $\beta$ -hydride elimination from  $[N-CH_3]$  (Figure 4). Surface methyl radicals generated from the pyrolysis of  $Me_3Ga$  can be removed as the stable  $CH_4$  molecule, which therefore reduces the carbon contamination in the resulting GaAs films.



**Figure 4** Decomposition mechanism of compound **18**: (i)  $\beta$ -hydride elimination from  $[\text{N}-\text{CH}_3]$ ; (ii) removal of surface methyl radicals.

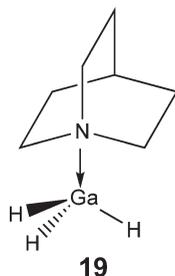
Diethyl-tertiarybutylarsine ( $\text{Bu}^t\text{AsEt}_2$ ) and diethyl-isopropylarsine ( $\text{Pr}^i\text{AsEt}_2$ ) are alternative precursors to  $\text{AsH}_3$ , which combine the advantages of the lower intrinsic toxicity associated with trialkylarsines with the use of  $\beta$ -hydride eliminating groups.<sup>116</sup> However,  $\text{Bu}^t\text{AsEt}_2$  and  $\text{Pr}^i\text{AsEt}_2$  have only low vapor pressures of 3.6 and 6.1 torr, respectively, at 25 °C. The use of  $\text{Bu}^t\text{AsEt}_2$  and  $\text{Pr}^i\text{AsEt}_2$  in combination with  $\text{Me}_3\text{Ga}$  or  $\text{Et}_3\text{Ga}$  resulted in p-type GaAs layers with 77 K mobilities in the range  $3,500\text{--}4,100\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ , indicating that these As sources do not provide sufficient active hydrogens to remove all the carbons during MOCVD. The incorporation of Ga and In into (GaIn)As grown by MOCVD used the group V precursors  $\text{AsH}_3$ ,  $\text{Bu}^t\text{AsH}_2$ , and  $\text{Bu}^t\text{AsEt}_2$ .<sup>117,118</sup> Multilayer structures of (GaIn)As layers were grown alternately with  $\text{AsH}_3$  and either  $\text{Bu}^t\text{AsH}_2$  or  $\text{Bu}^t\text{AsEt}_2$ . It was found that the In/Ga ratio in the solid increased with decreasing number of As-H bonds in the group V precursor. These differences in In/Ga incorporation were attributed to increased binary growth rate of InAs in the alternately grown (GaIn)As. The effect of increased In incorporation was greater when using  $\text{Bu}^t\text{AsEt}_2$ .

The vapor pressure of  $\text{R}_3\text{Al}$  compounds can be increased by replacing the methyl groups with bulky sterically hindered groups, such as *t*-butyl. These groups reduce the tendency of the  $\text{R}_3\text{Al}$  molecules to associate via bridging alkyl groups and  $\text{Bu}^t_3\text{Al}$  is monomeric. Thus, the vapor pressure of  $\text{Bu}^t_3\text{Al}$  is sufficient for MOCVD and high-quality AlGaAs layers have been grown from  $\text{Bu}^t_3\text{Al}$ ,  $\text{Et}_3\text{Ga}$ , and  $\text{AsH}_3$  at 650 °C.<sup>119</sup> Carbon was not detected in the resultant films, either by secondary ion mass spectroscopy (SIMS) or low-temperature (4 K) PL spectroscopy. The low levels of carbon in the AlGaAs layers grown using  $\text{Bu}^t_3\text{Al}$ ,  $\text{Et}_3\text{Ga}$ , and  $\text{AsH}_3$  are consistent with the high-quality Al films ( $\text{C} < 0.5\text{ wt.}\%$ ) grown from  $\text{Bu}^t_3\text{Al}$ .<sup>120</sup> The facile removal of the *t*-butyl radical from the substrate surface via  $\beta$ -hydride elimination affords Al films, which are carbon free (Figure 5).



**Figure 5**  $\beta$ -Hydride elimination from a coordinated *t*-butyl radical resulting in surface-bound hydrogen and isobutene.

A gallane–quinuclidine adduct (compound **19**) has been used as an alternative Ga source for the MOMBE growth of GaAs films.<sup>121</sup> The surface decomposition of compound **19** is similar to the related alane adduct,  $[\text{AlH}_3\{\text{NMe}_3\}]$  **7**, and growth of GaAs is observed at much lower temperatures than those employed when Ga alkyl precursors are utilized.



Unlike the other group V elements, antimony has no stable hydride at room temperature. Because of the lack of a stable hydride, most of the antimonide-based III–V semiconductors are grown using  $\text{Me}_3\text{Sb}$ .<sup>122</sup> This source is chosen because of its ready availability and its high vapor pressure. High-quality GaSb layers were grown by MOCVD using  $\text{Me}_3\text{Ga}$  and  $\text{Me}_3\text{Sb}$  at relatively high growth temperatures ( $\sim 600^\circ\text{C}$ ).<sup>123,124</sup> However, a range of alternative Sb precursors have been investigated in order to lower the growth temperature, which in turn should minimize interdiffusion between layers in heterostructures. Another problem with  $\text{Me}_3\text{Ga}$  and  $\text{Me}_3\text{Sb}$  is the possibility of carbon contamination due to methyl radicals. Epitaxial GaSb was deposited from  $\text{Me}_3\text{Ga}$  or  $\text{Et}_3\text{Ga}$  in combination with  $\text{Me}_3\text{Sb}$ ,  $\text{Et}_3\text{Sb}$ , or  $\text{Sb}(\text{NMe}_2)_3$  by LPCVD.<sup>125,126</sup> When using  $\text{Me}_3\text{Ga}$  as the Ga source, growth is kinetically limited in the temperature range  $560\text{--}640^\circ\text{C}$ , whereas with  $\text{Et}_3\text{Ga}$ , it is mass transport limited in the range  $525\text{--}640^\circ\text{C}$ . Pre-reaction between  $\text{Et}_3\text{Ga}$  and  $\text{Et}_3\text{Sb}$  or  $\text{Sb}(\text{NMe}_2)_3$  resulted in surface defects; however, featureless morphology was obtained for GaSb layers deposited from  $\text{Me}_3\text{Ga}$  or  $\text{Et}_3\text{Ga}$  and  $\text{Me}_3\text{Sb}$ . The electrical properties of the resulting films were found to be optimal for layers grown with  $\text{Et}_3\text{Ga}$  and  $\text{Me}_3\text{Sb}$  or  $\text{Et}_3\text{Sb}$ , the most robust combination being  $\text{Et}_3\text{Ga}$  and  $\text{Me}_3\text{Sb}$ . Alternatively,  $\text{Et}_3\text{Ga}$  and  $\text{Bu}^t\text{SbMe}_2$  were used to deposit GaSb films on GaAs substrates.<sup>127</sup> This combination provided more efficient growth and good island nucleation resulting in thick layers.

Tris(dimethylamino)stibine,  $\text{Sb}(\text{NMe}_2)_3$ , has been used, in combination with  $\text{Me}_3\text{In}$ , to grow high-quality InSb epitaxial layers at  $275\text{--}425^\circ\text{C}$ .<sup>128,129</sup> It was suggested that the decomposition of  $\text{Me}_3\text{In}$  may be accelerated by  $\text{Sb}(\text{NMe}_2)_3$  via a free-radical mechanism and the carbon contamination reduced by reaction of  $\text{NMe}_2$  radicals with methyl radicals to give the stable volatile molecule  $\text{NMe}_3$ . However, a more complex mechanism, such as that described above for compound **18** and  $\text{Me}_3\text{Ga}$  (Figure 4), may occur. InSb films grown from  $\text{Me}_3\text{In}$  and  $\text{Bu}^t\text{SbMe}_2$  were similar to those deposited from  $\text{Sb}(\text{NMe}_2)_3$ .<sup>128</sup> Epitaxial layers of ternary and quaternary alloys, such as GaAsSb,<sup>130</sup> GaInAsSb,<sup>131</sup> InAsSb,<sup>132</sup> and AlGaAsSb<sup>135</sup> have been grown by MOVPE using a range of group III and V sources. The Sb sources utilized include  $\text{Me}_3\text{Sb}$ ,  $\text{Sb}(\text{NMe}_2)_3$ , and  $\text{Bu}^t\text{SbMe}_2$ , and the As source employed was  $\text{Bu}^t\text{AsH}_2$ . In general, the conventional trimethyl compounds of the group III elements were used to deposit the alloys, although for InAsSb, triisopropylindium was used.

The growth of AlSb and other AlSb-containing alloys has proved to be the most challenging of all the antimony-containing III–V semiconductors. This difficulty is primarily due to the lack of suitable sources for the growth of AlSb at low temperatures and the resulting incorporation of excess amounts of carbon. The strong Al–C bond and lack of active hydrogen species, necessary for the removal of methyl radicals, results in heavy carbon contamination. However, AlSb films have been grown at  $500^\circ\text{C}$  and 76 torr using trimethylamine alane **7** and  $\text{Et}_3\text{Sb}$ .<sup>133</sup> The ternary alloy, AlGaSb, was grown from  $\text{Bu}^t_3\text{Al}$  and either  $\text{Me}_3\text{Sb}$  or  $\text{Et}_3\text{Sb}$  by low-pressure MOCVD.<sup>134</sup> The carbon contamination in the resulting films was significantly lower than that observed in layers grown with  $\text{Me}_3\text{Al}$ ,<sup>135</sup> due to the  $\beta$ -hydride elimination pathway.

### 12.01.2.2 Single-source Organometallic III–V Precursors

An alternative method for lowering the growth temperature of III–V semiconductors is to use single-source precursors, which already contain an M–E ( $M = \text{Al, Ga, In}$ ;  $E = \text{N, P, As, Sb}$ ) bond at the core of the molecule, with various other ligands attached to each of the elements. The desired reaction pathway involves adsorption of the

precursor without breaking the M–E bond but with loss of the ancillary ligands. Single-source precursors potentially display a range of advantages over conventional MOCVD precursors, including the following.

- (i) Reduced toxicity (AsH<sub>3</sub>, PH<sub>3</sub> are eliminated from the CVD process).
- (ii) Low-temperature growth is possible.
- (iii) Pre-reaction is limited as there is only one precursor.
- (iv) Air and moisture stability is possible.

However, single-source precursors have yet to be commercialized for the growth of III–V semiconductors due to their disadvantages, including the following.

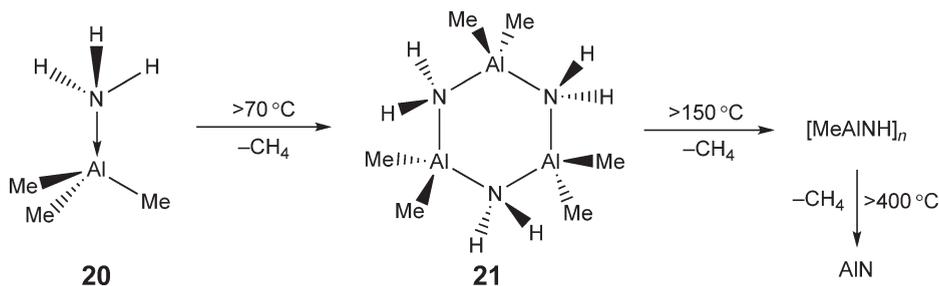
- (i) Low volatility, which renders the use of established MOCVD equipment difficult.
- (ii) Epitaxial growth may be prevented by the low surface mobility of polynuclear decomposition fragments.
- (iii) The control of stoichiometry can be difficult using single-source precursors, particularly in the growth of ternary and quaternary materials, for example In<sub>x</sub>Ga<sub>1-x</sub>As<sub>x</sub>.

Single-source organometallic precursors for III–V semiconducting materials have been reported. Many of the precursors to GaAs and GaP were reported prior to 1994, as discussed in a number of reviews<sup>2,7-9</sup> and mentioned in chapter 11, volume 1 of COMC (1995).

### 12.01.2.2.1 Group III nitride precursors

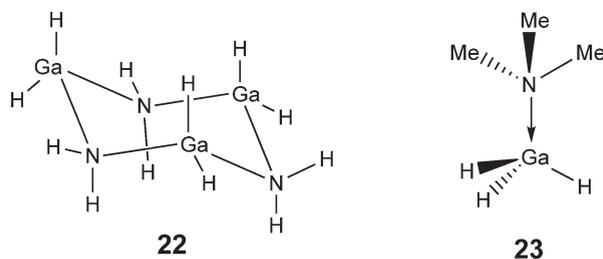
The trimethylaluminum–ammonia adduct [Me<sub>3</sub>Al{NH<sub>3</sub>}] **20** was prepared by bubbling NH<sub>3</sub> through a solution of Me<sub>3</sub>Al in pentane.<sup>136,137</sup> The adduct **20** was investigated as a single-source precursor to AlN in an attempt to achieve low growth temperatures while retaining sufficient precursor volatility.<sup>136</sup> Compound **20** is monomeric and thus expected to have a high vapor pressure for use in MOCVD. Indeed, polycrystalline AlN films were deposited on Si(100) substrates from **20** at 400–800 °C. In contrast, epitaxial AlN layers, suitable for use as buffer layers, were deposited from **20** on sapphire(0001) substrates at 900 °C. The carbon contamination in the resulting AlN films was low (0.6–4.8 at.%), which was attributed to the efficient removal of CH<sub>3</sub> radicals by active hydrogen deriving from the adjacent NH<sub>3</sub> groups attached to the Al center. Although the mechanism for the growth of AlN from **20** has not been established, it is likely to proceed, as shown in Scheme 7, via [Me<sub>2</sub>AlNH<sub>2</sub>]<sub>3</sub> **21**. This mechanism is different to that proposed for the gas-phase chemistry of Me<sub>3</sub>Al and NH<sub>3</sub> by FTIR and XPS studies (Section 1.2.1.1);<sup>23</sup> however, sequential elimination of alkane and the formation of amide (NH<sub>2</sub>) species is common to both proposed mechanisms. MOCVD of related complexes, of the type [Me<sub>2</sub>AlN(H)R]<sub>2</sub> (**1**, R = Bu<sup>t</sup>; **2**, R = Pr<sup>i</sup>), afforded AlN films between 700 and 800 K.<sup>37</sup> Carbon contamination was observed in the resulting films and was mainly attributed to the methyl groups bonded to the aluminum atoms using mass analysis experiments. The *t*-butyl group was found to be a superior substituent to isopropyl since the deposition temperature was lowered by 50 K, less carbon was incorporated, and higher nitrogen content was observed. This is probably due to the β-hydride elimination of the *t*-butyl group being more effective at removal of methyl radicals from the growth surface.

The molecular precursor cyclotrigallazane, [H<sub>2</sub>GaNH<sub>2</sub>]<sub>3</sub> **22**, has no organic substituents, and should therefore yield carbon-free GaN. Compound **22** was synthesized from the reaction of [H<sub>3</sub>Ga{NMe<sub>3</sub>}] **23** and ammonia.<sup>138</sup> Wells and co-workers later published the formation of **22** from LiGaH<sub>4</sub> and NH<sub>4</sub>X (X = Cl, Br).<sup>139</sup> The use of LiGaH<sub>4</sub> in place



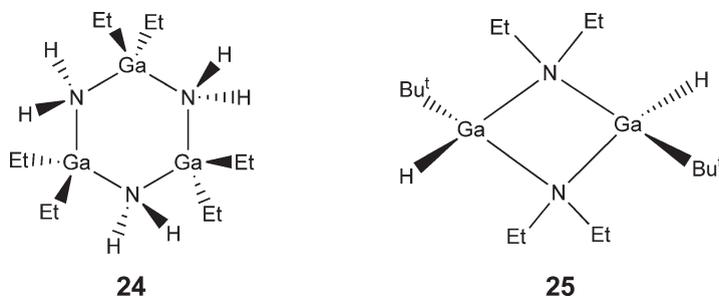
Scheme 7

of **23** eliminates one synthetic step as compound **23** is prepared from  $\text{LiGaH}_4$ . The structure of **22** consists of alternating  $\text{H}_2\text{Ga}$  and  $\text{NH}_2$  units forming a six-membered  $(\text{GaN})_3$  ring which adopts a chair conformation.<sup>140</sup>



Pyrolysis of powdered samples of **22** under a range of conditions resulted in the formation of nanocrystalline GaN. The powder XRD data indicated that the nanocrystalline GaN had neither the pure wurtzite or pure zinc blende structure but a random arrangement of stacking planes with an equal amount of cubic and hexagonal planes.<sup>138</sup> Interestingly, changing the atmosphere of the pyrolysis from Ar to  $\text{N}_2$  to  $\text{NH}_3$  had no effect and the results obtained were the same. At  $900^\circ\text{C}$ , the nanocrystalline GaN slowly converted into the known wurtzite phase. It was suggested that the formation of metastable GaN with such a high percentage of the cubic phase was a result of a topochemical reaction in which hydrogen elimination occurs along a reaction coordinate established by the structure of compound **22**. Thin films of polycrystalline GaN were also deposited on Si(100) using precursor **22**. Powder XRD showed that the polycrystalline GaN films had the wurtzite structure. Under ammonothermal conditions, **22** can be converted to nanocrystalline GaN.<sup>141</sup>

The trimeric compound  $[\text{Et}_2\text{GaNH}_2]_3$  **24** has been prepared by the reaction of  $\text{Et}_3\text{Ga}$  with ammonia.<sup>142</sup> Crystalline GaN films have been grown by low-pressure MOCVD at  $500\text{--}700^\circ\text{C}$  from compound **24**. The films deposited at  $600^\circ\text{C}$  are crystalline without cracks but with not a very smooth surface. The relatively low carbon content ( $\sim 2\%$ ) in the resulting films is probably related to the facile evolution of ethylene via  $\beta$ -hydride elimination (Figure 2). The synthesis of the related dimeric compound  $[\text{Bu}^t(\text{H})\text{Ga}(\text{NET}_2)]_2$  **25** was achieved by the addition of 4 equiv. of  $^t\text{BuLi}$  to  $[\text{Cl}_2\text{GaNEt}_2]_2$ .<sup>143</sup> Compound **25** was found to be air stable, although it decomposes at elevated temperatures. Preliminary CVD studies using **25** showed that gallium-rich films are formed, as  $\text{Et}_2\text{NH}$  is a facile leaving group. These results suggest that it would be necessary to add an external nitrogen source, such as  $\text{NH}_3$ , in order to deposit GaN films from compound **25**.<sup>143</sup>

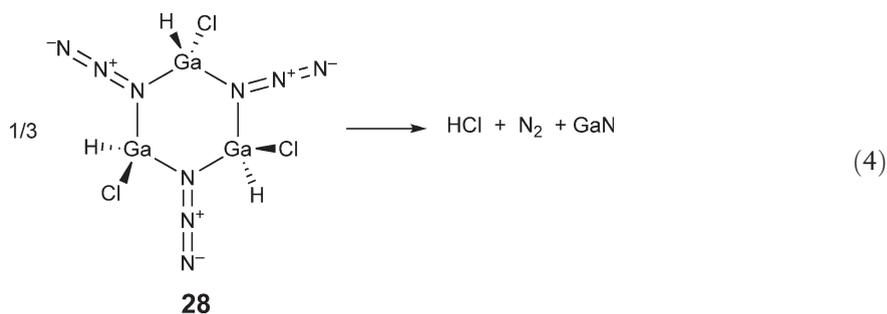


A series of precursors to group III nitrides that contain the azide ( $\text{N}_3$ ) ligand have been characterized. The azide group contains a preformed strong Ga–N bond and reduces the number of Ga–C and N–C bonds, which potentially minimizes the possibility of carbon incorporation into the material during growth. A simple and stable molecular source for GaN is  $[\text{H}_2\text{GaN}_3]$  **26**, which was prepared by the  $\text{LiGaH}_4$  reduction of  $[\text{Br}_2\text{GaN}_3]$ .<sup>144</sup> The deuterated analog  $[\text{D}_2\text{GaN}_3]$  **27** was synthesized in a similar manner from  $\text{LiGaD}_4$  and  $[\text{Br}_2\text{GaN}_3]$ .<sup>145</sup> Mass spectral data indicate that both **26** and **27** are trimeric. These complexes are volatile at room temperature and can be distilled at  $40^\circ\text{C}$  (0.20 torr) without decomposition. The decomposition pathway of compounds **26** and **27** represents one of the simplest chemical routes to GaN, as shown in Equation (3). Furthermore, only benign  $\text{H}_2$  or  $\text{D}_2$  and  $\text{N}_2$  byproducts are formed.

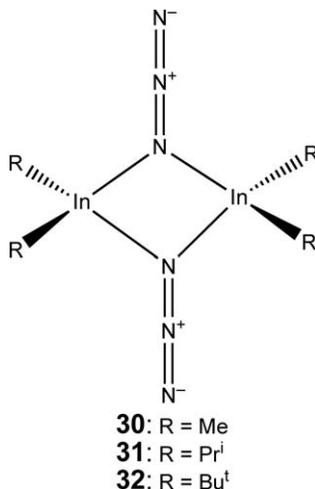


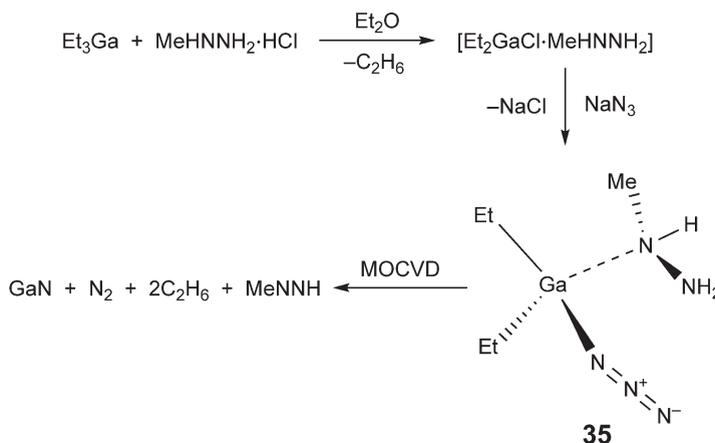
The significant vapor pressure of compound **26** allowed rapid mass transport of the precursor at 22 °C and the facile decomposition pathway resulted in film growth at temperatures as low as 200 °C. Epitaxial GaN films were deposited from **26** at 650 °C via LPCVD.<sup>146</sup> The growth rate of the GaN films deposited was 800 Å min<sup>-1</sup>. Despite these excellent growth properties, the high reactivity of **26** necessitates careful manipulation of the neat product, as a vigorous exothermic decomposition can result.

The perdeuterated derivative **27** is thermally more robust than **26** and thus easier to handle.<sup>145</sup> Gallium nitride films were grown from compound **27** on Si(111) substrates via AlN buffer layers using gas-source MBE. Monocrystalline wurtzitic GaN films were obtained at substrate temperatures as low as 275 °C. The high degree of crystallinity of GaN grown under these conditions is unusual at such low temperatures. Films grown at 400–500 °C from **27** were also monocrystalline and highly orientated. Depositions of compound **27** in the presence of atomic N at 650 °C resulted in epitaxial films of cubic and hexagonal structures. The related complex [HClGaN<sub>3</sub>]<sub>n</sub> **28** comprises [HClGaN<sub>3</sub>]<sub>3</sub> trimers in the vapor phase, which decompose readily at low temperatures by elimination of HCl and N<sub>2</sub> (Equation (4)).<sup>147</sup> GaN layers on sapphire and Si substrates were deposited from this compound. However, [H<sub>2</sub>GaN<sub>3</sub>] is a superior precursor as no HCl is eliminated. The halide compound [Cl<sub>2</sub>GaN<sub>3</sub>] was prepared from [Cl<sub>3</sub>Ga{N<sub>3</sub>SiMe<sub>3</sub>}] and has also been used to grow high-quality GaN films on Si.<sup>148</sup>



A range of dialkyl group 13 azides have been synthesized and employed as precursors to the respective nitrides. Polymeric [Me<sub>2</sub>GaN<sub>3</sub>]<sub>n</sub> **29** was synthesized by the reaction of [Me<sub>2</sub>GaCl] with NaN<sub>3</sub>.<sup>149</sup> Thin polycrystalline GaN films with strong (0002) preferred orientation were deposited from compound **29** at 450–650 °C via LPCVD.<sup>149</sup> Films were deposited on GaAs(100), GaAs(111), sapphire(0001), and quartz. At higher temperatures, cracks were evident on the surface of the GaN films. The indium analog, [Me<sub>2</sub>InN<sub>3</sub>]<sub>2</sub> **30**, is dimeric, and was prepared from the reaction of Me<sub>3</sub>In with HN<sub>3</sub>.<sup>150</sup> InN thin films were deposited from **30** on Si(111) substrates at 350–450 °C by LPCVD. The films were shown to be nitrogen-deficient InN (In:N ≈ 1:0.6) by XPS with high surface impurity concentrations (C 20%, O 27%). Powder XRD showed that the films were polycrystalline with the expected hexagonal wurtzite structure. The related compounds [R<sub>2</sub>InN<sub>3</sub>]<sub>2</sub> (**31**, R = Pr<sup>i</sup>; **32**, R = Bu<sup>t</sup>) have been used to prepare InN fibers via thermolysis in refluxing diisopropylbenzene in the presence of H<sub>2</sub>NNMe<sub>2</sub>.<sup>151</sup>

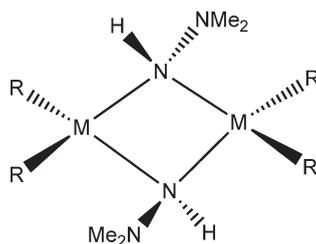




Scheme 8

Dibenzylaluminum and gallium azides, of the type  $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{MN}_3(\text{THF})]$  (**33**,  $\text{M} = \text{Al}$ ; **34**,  $\text{M} = \text{Ga}$ ), were investigated as precursors for the low-temperature synthesis of AlN and GaN.<sup>152</sup> However, pyrolysis studies indicated that both **33** and **34** decompose before becoming volatile and  $\text{C}_6\text{H}_5\text{CH}_2\text{-CH}_2\text{C}_6\text{H}_5$  was produced. In contrast, epitaxial *h*-GaN films were grown on Si(111) substrates from  $[\text{Et}_2\text{GaN}_3(\text{Me}(\text{H})\text{NNH}_2)]$  **35** via high vacuum MOCVD at 400–800 °C.<sup>153</sup> Compound **35** was prepared as shown in Scheme 8. The atomic ratio of Ga:N in the resulting GaN films was found to be 1:0.94 by XPS with minimal carbon incorporation (~0.1 at.%). The gas-phase products of the MOCVD reaction were analyzed by gas chromatography-mass spectroscopy (GC-MS), which revealed the presence of  $\text{N}_2$ ,  $\text{C}_2\text{H}_6$ , and MeNNH (Scheme 8). These results suggest that compound **35** undergoes protonation of the ethyl ligands by methylhydrazine to deposit GaN films. The related precursor  $[\text{Et}_2\text{GaN}_3(\text{Bu}^t\text{NH}_2)]$  **36** also afforded crystalline GaN thin films on sapphire(0001) and GaAs(001) substrates at 500–800 °C via MBE.<sup>154</sup> Compound **36** was also used for the growth of GaMnN thin films.<sup>154</sup>

Dimethylhydrazidodimethylgallium,  $[\text{Me}_2\text{GaN}(\text{H})\text{NMe}_2]_2$  **37**, was used to produce polycrystalline GaN thin films on GaAs(100) at 580 °C by LPCVD.<sup>155,149</sup> By scanning electron microscopy (SEM), the film had the appearance of precipitated particles, suggesting poor adhesion to the substrate. The poor morphology and film quality was attributed to Ga–N bond cleavage, which was observed to occur at 260 °C during pyrolysis studies. Thin films of AlN were grown on Si(100) and Si(111) substrates by LPCVD at 400–800 °C from  $[\text{R}_2\text{AlN}(\text{H})\text{NMe}_2]_2$  (**38**,  $\text{R} = \text{Me}$ ; **39**,  $\text{R} = \text{Et}$ ).<sup>156</sup> Polycrystalline AlN films were obtained on Si(111) using precursor **38** at 800 °C, whereas amorphous AlN films were afforded from **39** on Si(100) at lower temperatures.



**37**:  $\text{M} = \text{Ga}$ ;  $\text{R} = \text{Me}$

**38**:  $\text{M} = \text{Al}$ ;  $\text{R} = \text{Me}$

**39**:  $\text{M} = \text{Al}$ ;  $\text{R} = \text{Et}$

**40**:  $\text{M} = \text{Ga}$ ;  $\text{R} = \text{H}$

Pyrolysis of the related precursor  $[\text{H}_2\text{GaN}(\text{H})\text{NMe}_2]_2$  **40** on a supported inert oxide film,  $\text{HfO}_2$ , has been studied recently.<sup>157</sup> Compound **40** combines the advantages of both hydrido and hydrazido ligands and exhibits remarkable stability and volatility compared to most gallium hydride compounds. Initial studies showed that compound **40** decomposed to gallium metal when heated in a hot wall LPCVD reactor.<sup>158</sup> However, temperature-programmed reaction (TPR), AES, and isothermal reaction spectroscopy (IRS) using a time-of-flight mass spectrometer indicated

